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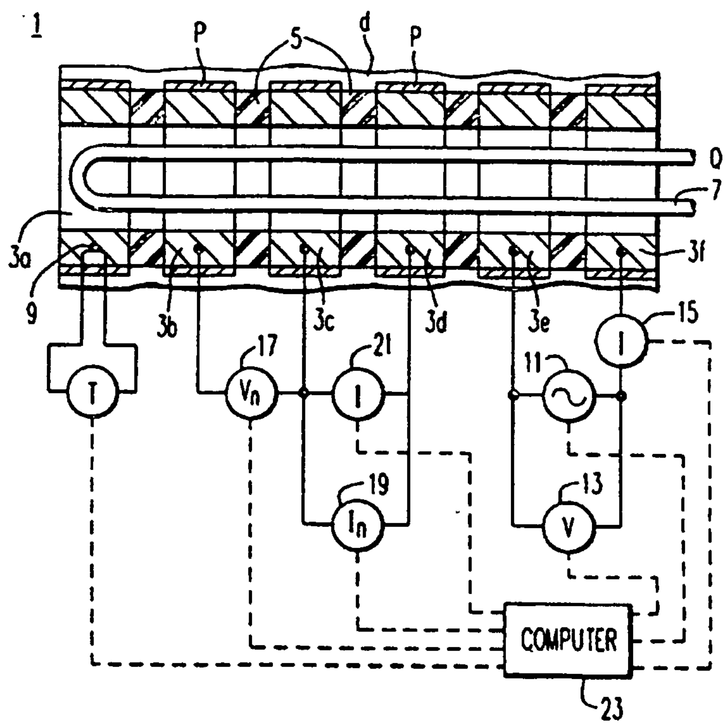
(54) Title: APPARATUS AND METHOD FOR REAL TIME CORROSION MONITORING IN HIGH TEMPERATURE SYSTEMS

(57) Abstract

Apparatus and method for producing real time indications of corrosion in high temperature processes utilizing a sensor having a plurality of electrodes spaced apart by high temperature insulators utilizing electrochemical noise indications from two parallel circuits having a common electrode and leg in each parallel portion of the circuit, the noise indications from the circuit being utilized to provide real time indication of corrosion and cooperating with signals indicative of operating parameters or the addition of corrosion inhibitors to maintain the corrosion rate within boundaries defined by the corrosion resistance of the materials used and thereby reduce the real time corrosion degradation while maintaining acceptable operating parameters.



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APPARATUS AND METHOD FOR REAL TIME CORROSION MONITORING IN HIGH TEMPERATURE SYSTEMS

BACKGROUND OF THE INVENTION

The subject of the invention is an apparatus and method or process for providing real time process condition monitoring and more particularly an apparatus and method or process for real time corrosion monitoring at high temperature.

Corrosion attack is an inherent problem when operating high temperature combustion equipment. See in this regard, G. A. Whitlow et al., "On-Line Materials Surveillance For Improved Reliability In Power Generation Systems," NACE 1991 Corrosion Conference, Paper 254. In view of the time over which boilers have been manufactured, it would be expected that corrosion problems have been effectively solved. This is not the case because the multiplicity of factors, which include continued upgrading of designs and the utilization of different fuels. The limitations of service materials are quickly revealed if the composition or temperature of the combustion gas is allowed to vary outside narrow operating limits. The consistent trend for improved thermal efficiency demands that combustion temperatures run ever higher and steam temperatures are also steadily increased. Operating margins which in the past were available to cope with temporary excursions in gas temperature or combustion have been eroded as improved control instrumentation allowed boilers to be maintained closer to their threshold limits. While scope for improvement still

exists, operating limits can be rapidly exceeded in large modern combustion plants. The results can be devastating and a great deal of work is in progress to prevent such occurrences.

The conventional approach to materials selection is largely based on previous experience in similar systems. In many cases, earlier equipment was smaller and operated at lower temperatures. New plants are typically designed by extrapolation from prior experience. However, many factors are changed when plant capacity is scaled up. For example, the feed system design on a modern unit may have to be adjusted considerably to cope with additional fuel capacity and more stringent environmental regulations. Most importantly, the volume of the combustion chamber may need to be increased. This frequently causes the gas flow profile to change, especially during periods of reduced load when it is necessary to produce steam at a relatively constant degree of superheat. The change from the proven unit produces a new generation of problems to be solved. The installation of low NO_x burners in an existing boiler can produce a similar effect. Staged combustion conditions may promote tube wall sulfidation, wastage or molten salt attack in equipment which previously had not exhibited damage.

Two methods have been used traditionally to combat these problems. The simplest method is to use more corrosion resistant tube material. However, the approach is expensive and may require a shutdown to allow the furnace to be retubed. An alternative is to try to control the combustion environment within tolerance limits of the material already in use. This approach is attractive because it is less expensive and, if successful, may not require an outage to replace tube material. It is desirable to better understand the causes of failure prior to the specification of an alternative material, to avoid a wasted investment with the use of a less than satisfactory alloy. Experience has shown that low cost materials

have proven adequate for ever more arduous service when used in conjunction with improved control or with corrosion inhibiting additives.

In assessing the corrosivity of combustion gases, it is normal practice to use a combination of inspection, weight loss coupons and metallography to formulate remedial measures and establish their effectiveness. Such inspection often requires the boiler be taken out of service and metallography may require the removal of a sample section of tubing. Neither method is capable of providing an instantaneous or real time indication of the rate at which tube wall thickness is affected in service. This disadvantage is unsatisfactory on two counts: first, results are delayed allowing tube wall thickness reduction to continue; and second, because results take time to become available and only the average corrosivity of the system is established. The effects of harmful transient conditions which cause the majority of attack are not evident and hence their causes are not remedied. The conventional route to materials selection and appraisal is therefore severely limited by the extent to which it can enable the design and operation of combustion equipment to be optimized.

Modern electrochemical corrosion monitoring methods employed at low temperature are disclosed in U.S. 4,575,679 and UK patent 2,118,309B, but have not been useful in applications involving high temperatures as high as 500°F.

SUMMARY OF THE INVENTION

Among the objects of the invention may be noted the provision of an apparatus and method for monitoring corrosion on a real time basis when temperatures are over 500°F to provide continuous indication of the rate of corrosion or wastage and track transient increases in the rate of attack to link them directly to the combustion environment prevailing at the time and maintain variability in corrosion rate with boundaries defined by the corrosion resistance to the materials used.

In general, a method of controlling a process parameter to limit the real time material degradation of a component in a process stream operating above 500°F , when made in accordance with this invention, comprises the steps of:

providing a sensor having a plurality of spaced apart plates formed from the same material as the component, the plates being spaced apart by electrical insulators and being exposed to said process stream;

maintaining the sensor generally at or near the temperature of the component;

controlling the process or adding a corrosion inhibitor in response to a signal from the sensor indicative of at least one of the following: the electrochemical current noise, the electrochemical potential noise to thereby reduce the real time degradation of the component.

The apparatus or sensor for monitoring real time corrosion at temperatures above 500°F when made in accordance with this invention comprises three electrodes separated by high temperature insulators. The electrodes are disposed in a high temperature environment and have a first loop connecting two of the electrodes with a voltage meter capable of indicating the potential noise between the two electrodes and a second loop connecting the third electrode to an adjacent electrode with an amp meter capable of indicating the current noise between the two electrodes in the second loop.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention as set forth in the claims will become more apparent by reading the following detailed description in conjunction with the accompanying drawings, wherein like reference numerals refer to like parts throughout the drawings and in which:

Figure 1 is a schematic view of a sensor utilized to determine real time corrosion in a high temperature application;

Figure 2A shows solution resistance vs time;

Figure 2B shows charge transfer resistance vs time;

Figure 2C shows coupling current vs time;

Figure 2D shows potential noise vs time;

Figure 2E shows current noise vs time;

Figure 2F shows temperature vs time;

Figure 3 shows a corrosion circuit with a alternating power source imposed thereon; and

Figure 4 is a schematic view of a municipal solid waste incinerator having a high temperature real time corrosion sensor which controls a corrosion inhibitor additive injection system.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the drawings in detail and in particular to Figure 1 there is shown an apparatus or sensor 1, which is installed in a high temperature environment to obtain real time indications of corrosion. The apparatus or sensor 1 comprises a plurality of electrodes 3a, 3b, 3c, 3d, 3e and 3f generally made of the same material as that used within a high temperature process that operates above about 500°F, for example the outer surface of superheater tubes in a boiler wherein the corrosion is ascribed to processes such as molten salt damage, high temperature sulfidation, oxidation and chlorine or HCl attack and other high temperature corrosion processes. While superheater tubes are used as an example, the process is applicable to other convection section tubing, radiant section membrane tube walls, high temperature gas turbine components, gasification systems, fuel cells, chemical plant process heaters and similar types of high temperature combustion and process plant installations. The electrodes 3a-3f are separated from each other by a temperature resistant electrically insulating material 5. A heat transfer conduit 7 or other heat transfer means is provided, if required, to maintain the electrodes 3a-3f at the same metal temperature as the process element by either adding or removing heat Q as required. Material from the process forms a deposit d on

the electrodes 3a-3f and corrosion products p form on the surface of the electrodes 3a-3f. A thermocouple 9 or other temperature measuring device is installed in one of the electrodes 3a to measure and supply a signal for controlling the temperature T of the electrodes 3a-3f. Two electrodes 3e and 3f may have a device 11 for supplying an alternating current electrically connected across them and this circuit also incorporates means for measuring the voltage and current 13 and 15 respectively.

Three of the electrodes 3b, 3c and 3d are electrically connected to form two parallel circuits or loops with one of the electrodes 3c being common to both circuits or loops. One of the circuits or loops has a volt meter 17, which indicates changes in voltage or voltage or potential noise, V_n, while the other circuit or loop has an amp meter 19 which indicates changes in current or current noise, I_n, and an amp meter 21 which indicates the average current, I, in the circuit or loop. These current indications may be taken from a single amp meter, but are illustrated by two different amp or current meters. The various indications may be in analog or digital form so that they can be sent to a computer 23, which can perform various mathematical operations on the indications to put them in forms which are easily compared with previous indications so the changes in the indications become apparent and real time corrosion rates or changes in corrosion rates can be determined.

Figure 3 is an equivalent circuit to the circuit connecting electrodes 3e and 3f, wherein, solution resistance, R_s, the resistance of the corrosive compound is the resistance portion of an equivalent circuit and includes the capacitance of the electrodes, C_{dl}, and the resistance to transfer of the charge, R_{ct}, together with a dilution couplent, W, when an alternating power supply 11 is incorporated in the circuit. The solution resistance, R_s, shown in Figure 2A is plotted against time and is taken from a sensor 1 installed adjacent a superheater tube in a waste heat boiler, wherein the flue gas is the

result of burning solid municipal waste. Increases in solution resistance are usually related to an approach of the onset of corrosion.

Potential noise, V_n, is the change of potential indicated by the volt meter 17, shown in Figure 1. Potential noise is the change in voltage generated by the electrochemical corrosion of the electrodes 3 without applying any external power to the electrodes. Figure 2D shows the variation in potential noise over time. Increases and decreases in potential noise are indicative of the onset of corrosion.

Current noise, I_n,I is the change in current indicated by the amp meter 21 and is generated by the electrochemical corrosion of the electrodes without applying any external power. Figure 2E shows the current noise over an extended period of time. Increases in current noise, I_n, are related to an increase in electrochemical corrosion activity (rate) on the surface of the sensor elements.

Resistance noise, R_n, is the resistance value calculated by Ohms law utilizing simultaneous changes in potential noise, V_n, and current noise, I_n. The resistance noise, R_n, is inversely proportional to the rate of corrosion in the sensor 1 herein described and provides information similar to charge transfer resistance or polarization resistance when electrolytes are the active corrosive mechanism. A decrease in the resistance noise value, R_n, is indicative of an increase in corrosion rate and this can be related by Faraday's Law to a rate of metal loss.

One or more of the signals indicative of corrosion can be utilized in conjunction with operating parameters such as temperature, pressure, percent of O_2, CO or CO_2, on line analysis or other operating parameters to control the process and thus maintain the required operating parameters within acceptable limits and minimize the corrosion within the acceptable operating limits reacting in real time thus taking into account real time

corrosion and transient conditions which cause the majority of the corrosion. Such a control can react to the onset of corrosion, providing a step improvement in control of high temperature processes.

Referring now to Figure 4, there is shown a municipal solid waste incinerator 31, wherein solid municipal waste or other combustible material is fed into a rotary combustor 33 and burned. The products of combustion pass from the rotary combustor 33 to a waste heat boiler 35 having a superheater portion 37. The products of combustion passing over the superheater 37 are not only at high temperature, but often contain such corrosive elements ascribed to processes such as molten salt damage, high temperature sulfidation, oxidation and chlorine or HCl attack and other high temperature processes.

Operating parameters are governed by the requirements of the turbine (not shown) and local air pollution standards, so that in order to minimize corrosion, corrosion inhibiting additives such as dolomite, lime, limestone, magnesia or other corrosion inhibiting substances are added to the combustible solid waste as it enters the rotary combustor 33. The corrosion inhibiting additives are fed to the inlet end of the combustor via a pneumatic line 39 having a valve 41 or other means governing the rate or amount of additives supplied to the combustor. The valve 41 is regulated by the indications produced by the sensor 1.

One or more of the signals indicative of corrosion can be utilized by the computer 23 to operate the valve 41 and govern or control the amount or the rate at which corrosion inhibiting additives are supplied to the combustor 33 to assure that corrosion is maintained at a very low level with a minimum amount of corrosion inhibiting additives being supplied. The additives reduce the efficiency of the unit, are expensive and add to the amount of ash so that keeping the quantity added as low as possible substantially reduces operating costs and

still protects the components from high temperature corrosion.

In another practice of the method of the present invention, real time corrosion in water cooled and gas cooled nuclear reactors may be monitored. Thus, for example, real time corrosion may be monitored on-line at nominal temperatures of about 650°F or more in coolant circuits of pressurized water nuclear reactors or at nominal temperatures of about 1000°F or more in boiling water nuclear reactors.

While the preferred embodiments described herein set forth the best mode to practice this invention presently contemplated by the inventors, numerous modifications and adaptations of this invention will be apparent to others skilled in the art. Therefore, the embodiments are to be considered as illustrative and exemplary and it is understood that the claims are intended to cover such modifications and adaptations as they are considered to be within the spirit and scope of this invention.

What is claimed is:

1. A method of indicating real time condition of material and rate of material degradation of a component in a process stream operating above 500°F comprising the steps of:

providing a sensor having a plurality of spaced apart electrodes formed from the same material as the component;

spacing the electrodes apart with high temperature electrical insulators;

placing said sensor in said process stream;

maintaining the sensor generally at the temperature of the component;

receiving signals from the electrodes indicative of at least one the following: coupling current, current noise, potential noise and resistance noise; and

monitoring the indicative signals to establish variations with time, which indicate variations in the rate of material degradation of the component on a real time basis.

2. The method of claim 1, comprising the step of utilizing the current noise and potential noise signals to calculate resistance noise.

3. The method of claim 1, comprising imposing a alternating signal across two of the electrodes to determine the impedance thereof to assist in calculating solution resistance which can be utilized in conjunction with other indicative signals to indicate corrosion rate of the component on a real time basis.

4. The method of claim 1 and further comprising the step of utilizing the signals indicative of corrosion in conjunction with operating parameters of the process to keep the corrosion rate at a minimum and operate the process within acceptable operating parameters.

5. A method of controlling a process to limit the real time material degradation of a component in a process stream operating above 500°F, said method comprising the steps of:

providing a sensor having a plurality of spaced apart electrodes formed from the same material as the component;

providing electrical insulators between said electrodes;

exposing said electrodes to said process stream;

maintaining the sensor generally at the temperature of the component;

utilizing a signal from the electrodes indicative of at least one of the following: current noise, potential noise, coupling current, resistance noise and a signal indicative of at least one process parameter to operate the process within acceptable process limits and to maintain the corrosion rate within boundaries defined by the corrosion resistance of the materials used and thereby reduce the real time degradation of the component.

6. The method of claim 5, wherein the step of controlling the process in response to a signal from the electrodes comprises utilizing a response from a plurality of the following: current noise, potential noise, coupling current, and resistance noise and response from a plurality of process parameters.

7. The method of claim 5, wherein the step of controlling the process in response to a signal from the electrodes comprises utilizing signals indicative of the resistance noise.

8. The method of claim 5, wherein the step of controlling the process in response to a signal from the electrodes

electrodes comprises utilizing signals indicative of the potential noise, current noise and resistance noise.

9. The method of claim 5, wherein the step of controlling the process in response to a signal from the electrodes comprises utilizing signals indicative of the resistance noise, the potential noise and current noise wherein no external power is applied to the sensor electrodes utilized for producing these signals.

10. The method of claim 5, wherein the step of controlling the process parameter comprises utilizing a signal indicative of at least one of the following: temperature, pressure, percent of O_2 percent of CO and percent of CO_2 in the fluid stream passing over the component and sensor.

11. A apparatus for monitoring real time corrosion at temperatures above 500°F comprising three electrodes separated by high temperature insulators, the electrodes being disposed in a high temperature environment, a first loop connecting two of the electrodes with a voltage meter capable of indicating the potential noise between the two electrodes and a second loop connecting the third electrode to an adjacent electrode with an amp meter capable of indicating the current noise between the two electrodes so connected.

12. The apparatus of claim 11, wherein the loops comprise deposits from the environment which coat the electrodes and bridge the insulators.

13. The apparatus of claim 11, wherein the second loop is connected with an amp meter capable of indicating average current in the loop.

14. A method of evaluating on a real time basis, the addition of corrosion inhibiting additives to a combustion process comprising the steps of:

providing means for adding corrosion inhibiting additives to combustibles before combustion;

providing a sensor having a plurality of spaced apart electrodes formed from the same material as a component contacted by products of combustion;

spacing the electrodes apart with high temperature electrical insulators;

placing said sensor in contact with the products of combustion

maintaining the sensor generally at the temperature of the component;

receiving signals from the electrodes indicative of at least one the following: coupling current, current noise, potential noise and resistance noise; and

utilizing variations in at least one of the indicative signals to govern the addition of corrosion inhibiting additives to the combustibles to inhibit corrosion of the component.

15. The method of claim 14, wherein the step of receiving signals from the electrodes indicative of at least one of the following: coupling current, current noise, potential noise and resistance noise comprises receiving signals from a plurality thereof.

16. The method of claim 15, wherein the step of utilizing variations in the indicative signals comprises utilizing variations in a plurality of the indicative signals.

17. The method of claim 16, wherein the step of utilizing variations in the indicative signals to govern the addition of corrosion inhibiting additives includes utilizing the indicative signals to control the rate of adding corrosion inhibiting additives to the combustibles.

18. The method of claim 14, wherein the step of utilizing variations in the indicative signals to govern the addition of corrosion inhibiting additives includes utilizing the indicative signals to control the rate of adding corrosion inhibiting additives to the combustibles.

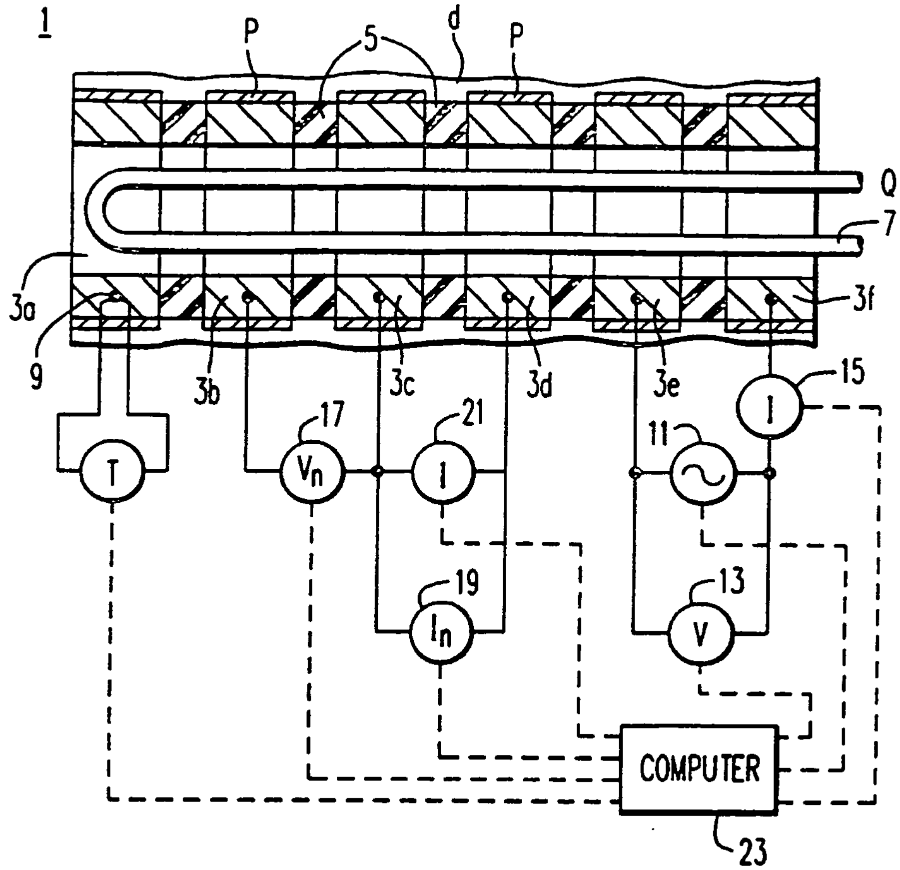
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FIG. 1

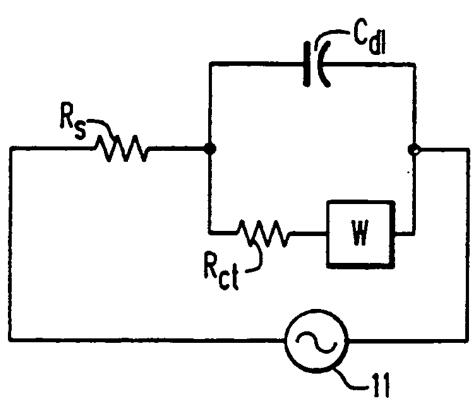
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FIG. 3

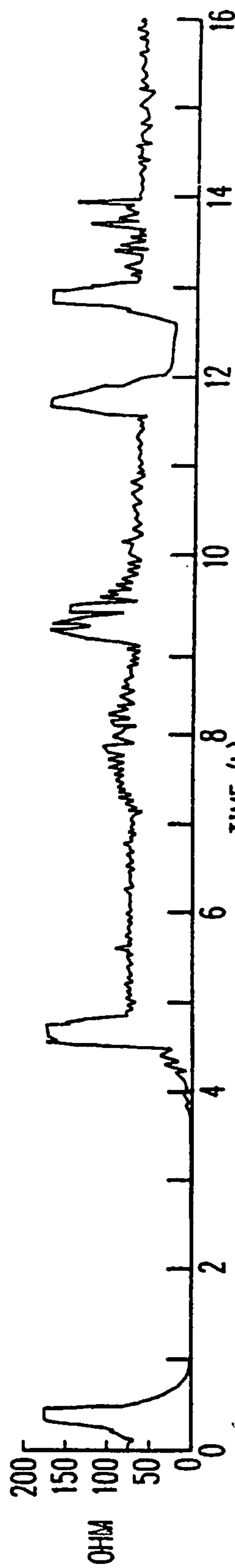

FIG. 2A

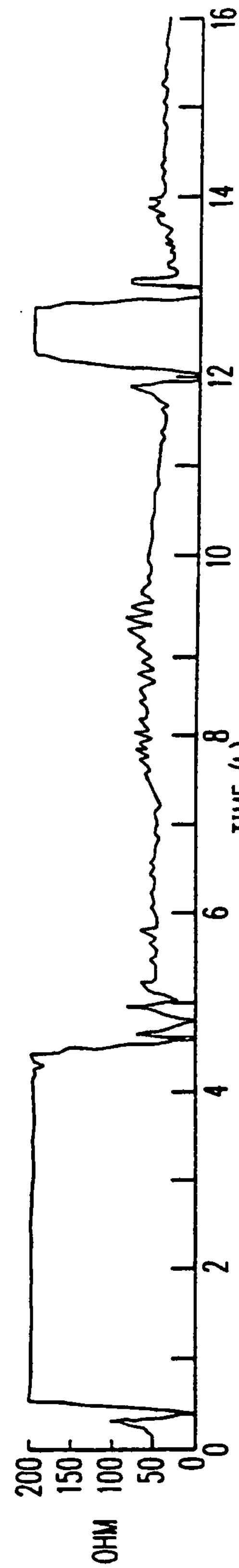

FIG. 2B

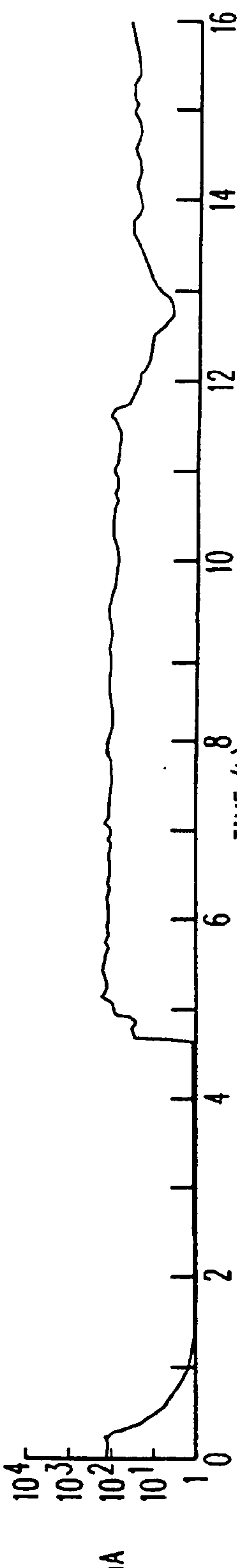

FIG. 2C

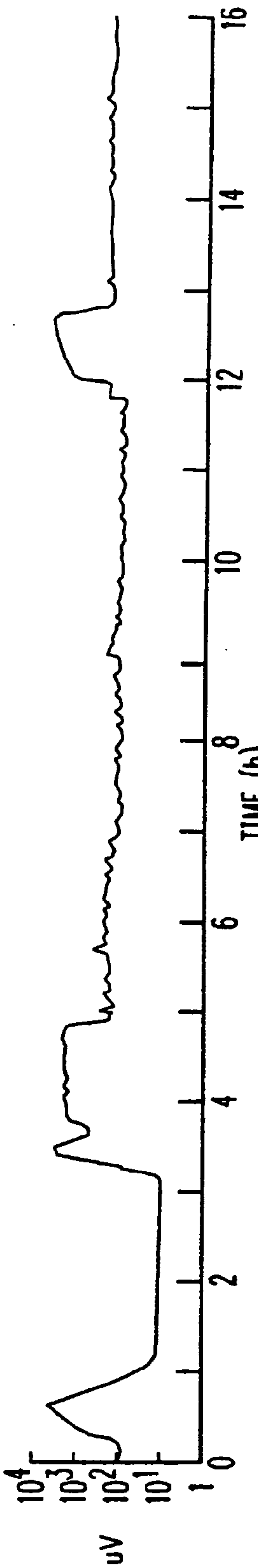

FIG. 2D

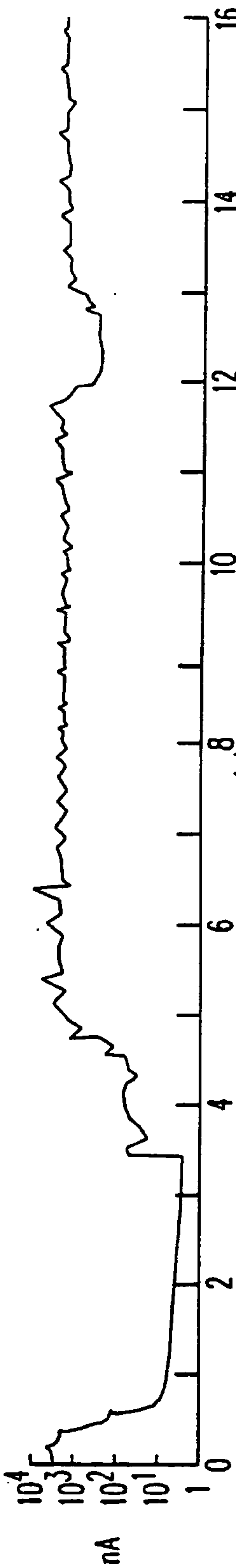

FIG. 2E

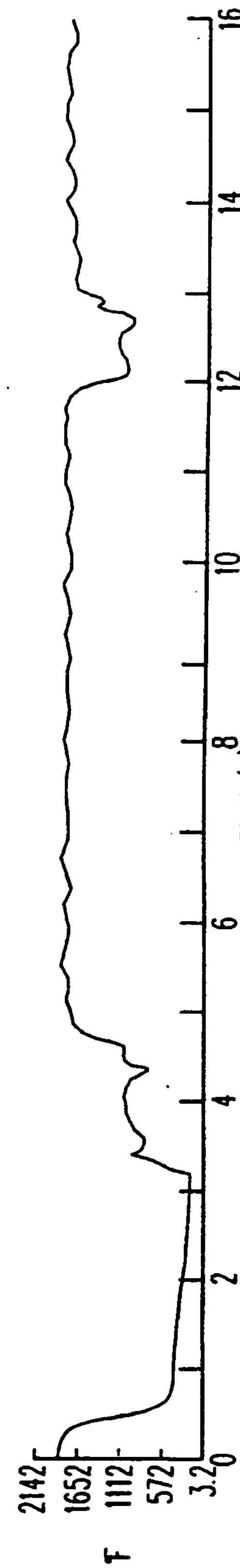

FIG. 2F

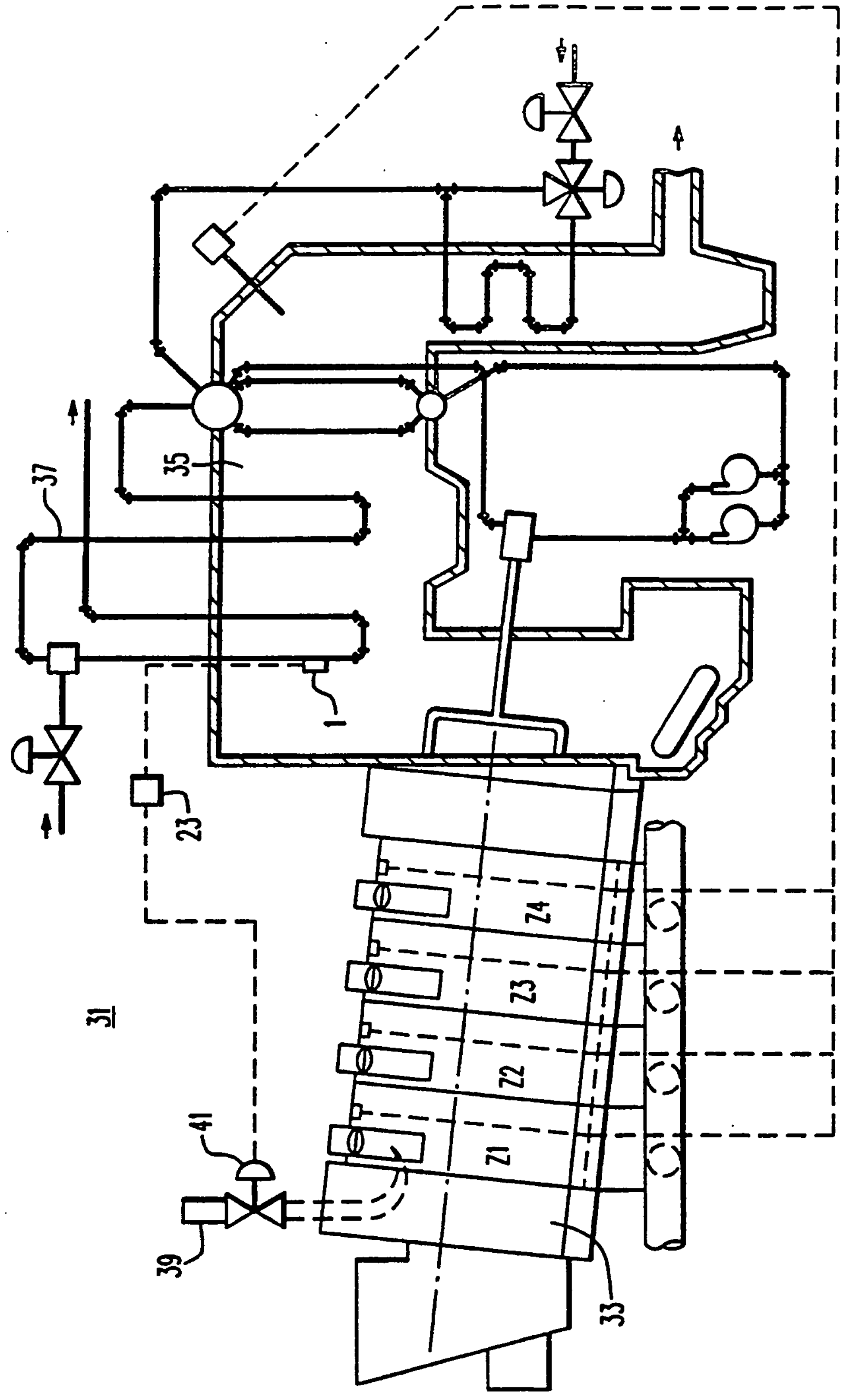

FIG. 4

INTERNATIONAL SEARCH REPORT

Inte: ›nal Application No
PCT/US 93/11374

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 G01N17/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	EP,A,0 052 388 (CISE) 26 May 1982 see abstract see page 6, line 26 - page 7, line 8; figure 1 ---	1 5,11,14
Y A	CORROSOIN 91 11 March 1991 , CINCINNATI pages 1 - 11 G.A.WHITLOW ET AL. 'On Line Materials Surveillance for Improved Reliability in Power Generation Systems' cited in the application see abstract see page 3, paragraph 4 see page 6, paragraph 2; figure 3 --- -/--	1 5,6,11, 14

[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
2 March 1994	15.03.94

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 16825 (CAPCIS MARCH LIMITED) 1 October 1992 see abstract; figures 1,2,8 ---	1,2
A	EP,A,0 330 549 (COMMISSARIAT A L'ENERGIE ATOMIQUE) 30 August 1989 see abstract see column 1, line 10 - line 16; figure 1 -----	1,4,5, 14,17,18

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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 93/11374

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